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Phosphorous Doping of Nanostructured Crystalline Silicon

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Abstract and Motivation

Nano-textured silicon, known as black silicon (bSi), is attractive with excellent photon trapping properties. bSi can be produced using simple one-step fabrication reactive ion etching (RIE) technique. However, in order to use bSi in photovoltaics doping process should be developed. Due to high surface aspect ration (22.25) of bSi to planar surface doping concentration might be slightly higher than on planar surfaces. Therefore, we conducted a study and present recent results of doping of bSi and compared their properties to planar Si. We doped planar, KOH-etched random pyramid and bSi surfaces with phosphorous (POCl3) in the temperature range 850-1000°C for 15 and 20 min, respectively. Sheet resistance measurements show slight differences in doping density between planar, KOH pyramidal and bSi structures. bSi samples have lower sheet resistance, pointing to higher doping density presumably due to the higher surface area. These results can be used to optimize doping processes for industrial application of bSi solar cells.

Samples Surface Structuring and Optical Properties

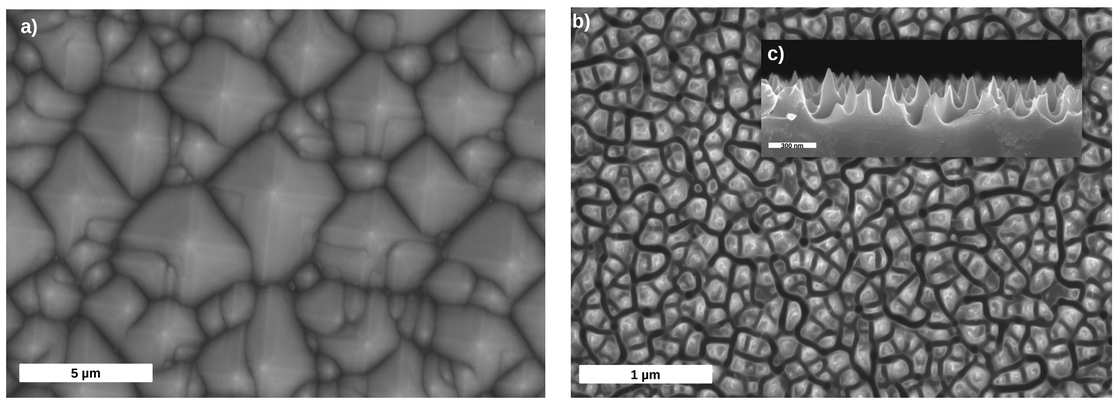


Fig.1. SEM images of a) KOH structured samples (top view), b) RIE black silicon structured samples (top view) and c) cross-section view

Wafer Cleaning and Surface Structuring

Prior to the doping process, we divided the wafers into three categories: planar (no surface modification), KOH-textured and RIE-textured.

Planar wafers were only cleaned with standard RCA cleaning procedure.

KOH wafers were immersed into buffered HF (bHF) solution to remove native oxide and then textured in 2% KOH solution with 7% IPA at 70°C for 50 min. They were then cleaned in a piranha solution to remove traces of the KOH solution.

RIE-textured wafers were dry etched (Pegasus SPS) in sulfur hexafluoride (SF_6) and oxygen (O_2) plasma with flow rates of 70 sccm and 100 sccm, respectively. The coil power was 3000 W and the platen power was set at 10 W. The etching time was 16 min. Details on RIE texturing presented in [1, 3]

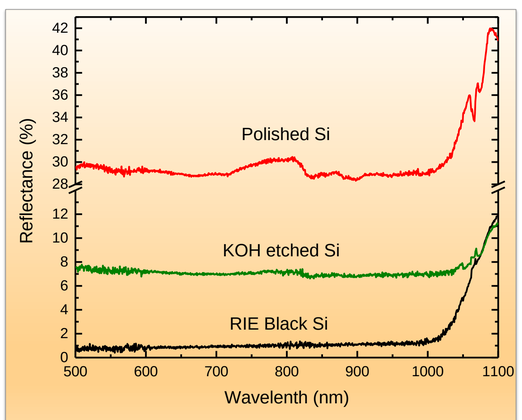
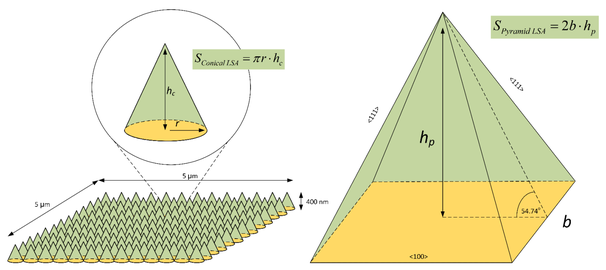


Fig. 2. **Experimental reflectance spectra** of polished, KOH etched and bSi samples before doping processes

Optical Properties of Samples

Optical measurement were carried out in integrated sphere setup. Reflectivity of polished Si wafer is round 30% while black silicon has in average reflectance below 0.5%.

Effect of surface area ratio



Surface morphology of KOH pyramidal microstructures and bSi nanostructures was investigated by SEM (Fig.1 a, b,c). Based on image processing and theoretical geometrical calculations we extracted the surface area ratio (SAR) as a ratio between the area of the lateral surfaces and their projected area. The difference SAR may explain the significantly lower sheet resistance of bSi particularly at lower doping temperatures, where the diffusion length is short.

Doping Process

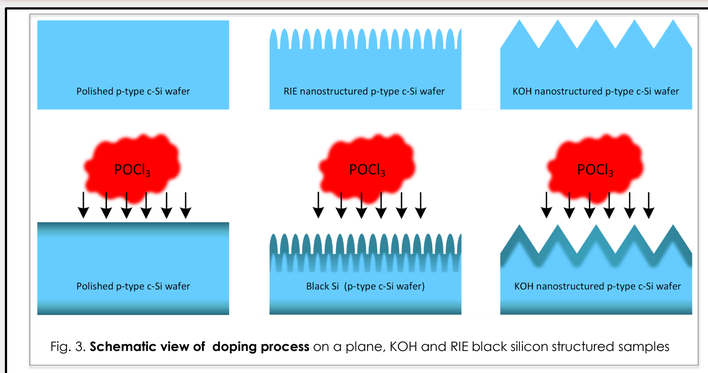


Fig. 3. **Schematic view of doping process** on a plane, KOH and RIE black silicon structured samples

- After optional texturing **all wafers were RCA** cleaned,
- divided in ten groups for 850°C, 875°C, 900°C, 950°C, 1000°C doping temperature 15 and 20 min doping time in combination.
- The wafers were loaded in a predep phosphorous diffusion furnace and doped using **$POCl_3$** as the dopant source.
- All the wafers were subjected to bHF etching and removal of phosphor-silicate glass (PSG) grown during the doping process.

Doping of the semiconductor in the pre-deposition process is a diffusion process, it is important to note the strong temperature dependency of the diffusivity [5]: $D = D_0 \exp\left(-\frac{E_A}{k_B T}\right)$, where D_0 is diffusion coefficient, E_A is the activation energy, k_B is the Boltzman's constant and T is the temperature in Kelvin. A linear pre-deposition process results in a complementary error-function doping profile [5] with the expected dose Q obtained from $Q = C_S \frac{2}{\sqrt{\pi}} \sqrt{Dt} \propto \exp\left(-\frac{E_A}{2k_B T}\right)$, where C_S is the surface doping concentration, and t is time. The sheet resistance of the doped layer is $R_\square = \frac{1}{qQ\mu_n}$, where q is the unit charge and μ_n the average electron mobility. It follows that the sheet resistance is expected to be strongly dependent on the temperature used in the doping process

Results and Analysis

Experiments with Temperature Dependent Doping

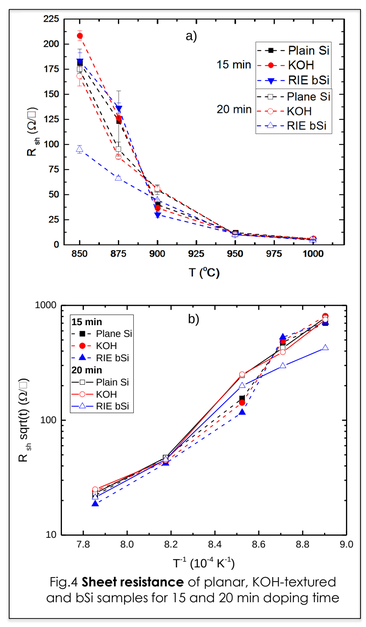


Fig.4 **Sheet resistance** of planar, KOH-textured and bSi samples for 15 and 20 min doping time

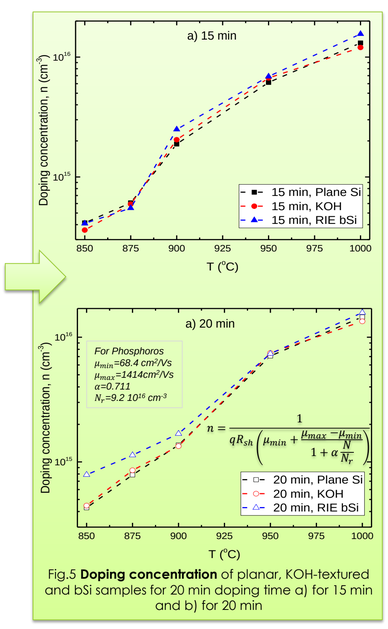


Fig.5 **Doping concentration** of planar, KOH-textured and bSi samples for 20 min doping time a) for 15 min and b) for 20 min

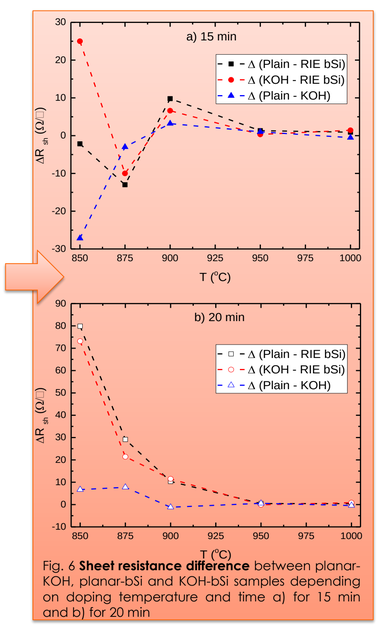


Fig. 6 **Sheet resistance difference** between planar-KOH, planar-bSi and KOH-bSi samples depending on doping temperature and time a) for 15 min and b) for 20 min

In Fig. 4 the sheet resistances measured for all doped samples are shown as a function of the reciprocal absolute doping temperature in a semi-log plot. The sheet resistance decreases rapidly as doping temperature is increased such that data points are almost on a straight line in Fig. 4. In Fig. 5 doping concentration was calculated from the values of sheet resistance according to the formula in the graph box. In Fig. 6 sheet resistance differentials between the different surfaces are shown as a function of doping temperature. In particular, for 20 min doping time it appears that the sheet resistance obtained on bSi is lower as those of the other two surfaces, which are very similar in sheet resistance value. Data from the 15 min experiment does not show the same unique tendency, perhaps because of lower total dose, which makes sheet resistance measurements more difficult and more prone to error.

Minority Carrier Lifetime Measurements

We used microwave detected photoconductivity method and setup from Freiberg Instruments for measurements of effective minority carrier. The resulting lifetime shown in Fig. 7 may be a result of Auger recombination. Auger recombination is most likely the dominant process, since the emitter are relatively highly doped at the interface at lower temperatures (850°C) and further decreases for bSi compared to KOH-textured and plane Si due to even higher dopant concentration and therefore higher Auger recombination in higher doped emitters.

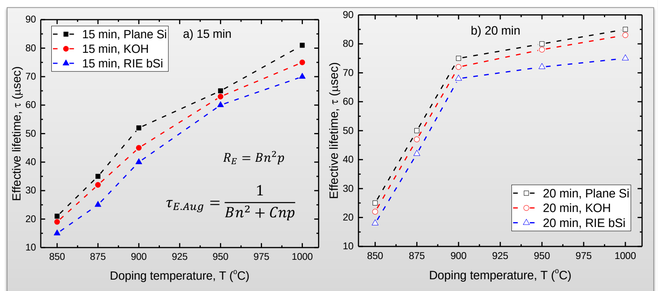


Fig. 7 **Effective carrier lifetime vs. doping temperature** a) for 15 min and b) for 20 min

Silvaco Athena Doping Process Simulation

Fig. 8 **Simulated cross-section** with and without doping. Red area corresponds to the junction depth (not to scale)

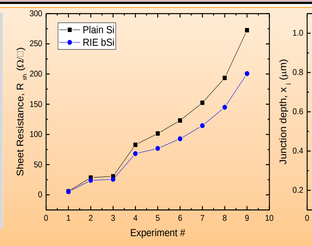


Fig. 9 **Sheet resistance** dependency for planar and nanostructured Si

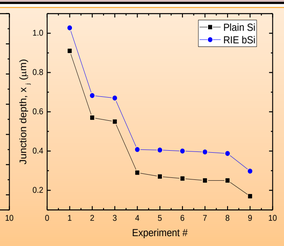


Fig. 10 **Junction depth** dependency for planar and nanostructured Si

Process	Process Temperature (Anneal), °C	Surface Concentration, cm^{-3}
1	1000 (1000)	5×10^{20}
2	985 (1000)	2×10^{20}
3	980 (1000)	2×10^{20}
4	975 (900)	8×10^{19}
5	975 (900)	7×10^{19}
6	975 (800)	6×10^{19}
7	975 (800)	5×10^{19}
8	950 (800)	5×10^{19}
9	930 (800)	1×10^{19}

Table 1. Simulated processes and parameters

In order to verify the results and investigate the observed differences may be explained solely by differences in the surface area and topology, simulations were carried out using the Athena Silvaco software. We used a simple phosphorus diffusion model, in which the dopant concentration was assumed constant and equal to the solid solubility at the Si surface. Defect induced diffusion was not taken into account. The results in Fig. 9 confirms the experimentally measured tendency that sheet resistance is significantly lower on bSi to planar Si. The relative diference in resistance between bSi and planar varies between 12 and 26% for the 9 diffusion process simulations. The junction in all cases is deeper for bSi compared to planar Si. This shows that the lower sheet resistance is not due to higher carrier density in the sheet but also a deeper junction.

Conclusions

In general, we show that nanostructured surfaces tend to have lower sheet resistance and therefore higher doping concentration in comparison to planar and KOH structured Si. With geometrical calculations and simulations we show that higher surface aspect ration causes higher doping and deeper junction. Due to dominating Auger recombination doped bSi has lower lifetime. In order to achieve the same order of doping as on planar surfaces, bSi doping process should be optimized.

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